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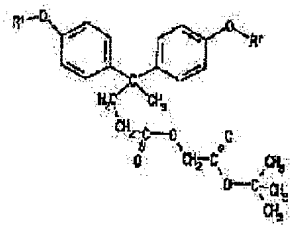
(54) DIPHENOLIC ACID T-BUTOXYCARBONYLMETHYL ESTER DERIVATIVE AND ITS PRODUCTION



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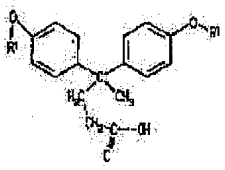

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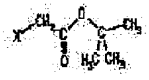

III

(57)Abstract:

PURPOSE: To obtain a new diphenolic acid t-butoxycarbonylmethyl ester derivative useful as a dissolution inhibitor for three-component type chemical amplification type resists.

CONSTITUTION: The objective diphenolic acid t-butoxycarbonylmethyl ester derivative of formula I (R1 is H, t-butyl, t-butoxycarbonyl, t-butoxycarbonylmethyl, 1-methyl-1-methoxyethyl, 2-tetrahydrofuranyl, 2-tetrahydropyranyl, methoxymethyl or t-butyldimethylsilyl), e.g. diphenolic acid t-butoxycarbonylmethyl ester. The compound of formula I is obtained by reaction between a compound of formula II or its derivative and an α-haloacetic acid ester of formula III (X is Cl, Br or I) in the presence of a base. When this compound is used as a dissolution inhibitor, sensitivity as well as resolution become sufficient because of sufficient dissolution contrast between light-exposed part and light-unexposed part; furthermore, pattern shape does not change with time.

LEGAL STATUS

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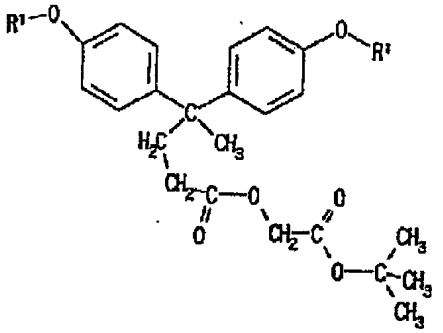
CLAIMS

[Claim(s)]

[Claim 1] Diphenolic acid-tert-butoxycarbonyl methyl ester derivative characterized by what is expressed with the following-ization 1;

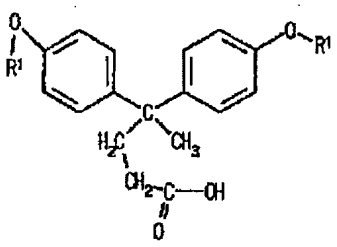
[Formula 1]



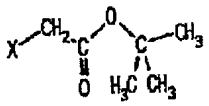
However, R1 in ** 1 One which is chosen from a hydrogen atom, tert-butyl, a tert-butoxycarbonyl radical, a tert-butoxy carbonylmethyl radical, a 1-methyl-1-methoxy ethyl group, a 2-tetrahydrofuranyl radical, 2-tetrahydropyranyl group, a methoxymethyl radical, and a tert-butyldimethylsilyl radical of radicals is expressed.

[Claim 2] The manufacture approach of the diphenolic acid-tert-butoxycarbonyl methyl ester derivative characterized by making alpha-halogenation acetic ester expressed with the diphenolic acid expressed with the following-ization 2 or its derivative, and the following-ization 3 react under existence of a base.

[Formula 2]



[Formula 3]



However, X in ** 3 expresses a chlorine atom, a bromine atom, or iodine atom.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the diphenolic acid-tert-butoxycarbonyl methyl ester derivative in which the property which was excellent when it used as a dissolution inhibitor of photoresist especially is shown, and its manufacture approach about a new dissolution inhibitor and its manufacture approach.

[0002]

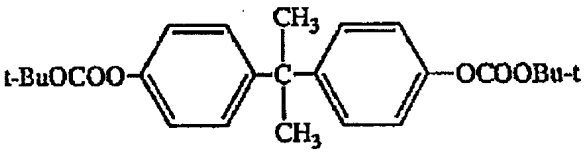
[Description of the Prior Art] the former -- resin -- the dissolution -- an inhibitor -- and -- an acid generator -- from -- becoming -- three -- a component -- a system -- chemistry -- magnification -- a mold -- a positive resist -- an ingredient -- setting -- a resist -- the film -- alkali -- a developer -- receiving -- a dissolution rate -- the dissolution -- an inhibitor -- controlling -- things -- [(dissolution rate of the part which irradiated the high energy line) -- / (dissolution rate of a non-irradiating part) (henceforth a dissolution rate ratio) -- large -- carrying out -- things --] -- a resist -- an ingredient -- ****** -- the engine performance -- especially -- being big -- effect -- doing -- things -- getting to know -- having -- **** -- . That is, when the part of the resist film at the time of irradiating high energy lines, such as ultraviolet rays, adds matter (dissolution inhibitor) which dissolves promptly to an alkali developer into a resist ingredient, the formation effectiveness of a resist pattern becomes very good.

[0003] Such a dissolution inhibitor has big effect on the engine performance of photoresist, and the 4-t-butoxycarbonyl biphenyl expressed with dibutoxy carbonyl bisphenol A expressed with the following-ization

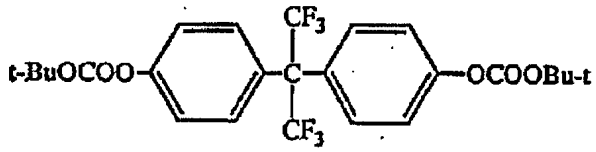
4, the dibutoxy carbonyl bisphenol F expressed with the following-ization 5, and the following-ization 6 as what is known from the former, t - butyl KORETO expressed with the following-ization 7, t - butyl deoxycholate expressed with the following-ization 8 are mentioned.

[0004]

[Formula 4]

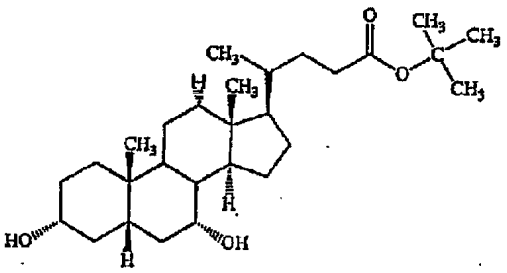


[Formula 5]

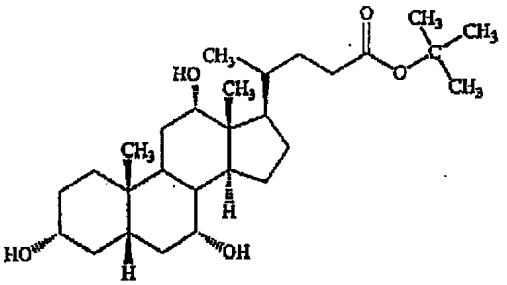


[Formula 6]

[Formula 7]



[Formula 8]



[0005] However, t-Bu or Bu-t is tertiary butyl among ** 4, ** 5, and ** 6. However, since the dissolution

contrast of the exposure section-unexposed part of a resist was not fully acquired, neither of these dissolution inhibitors could obtain sufficient definition and sensibility, and had the fault that the configuration of a resist pattern changed with aging.

[0006] For example, in the case of dibutoxy carbonyl bisphenol A and the dibutoxy carbonyl bisphenol F, although it has the big dissolution inhibition effectiveness to resin and has the description of being cheap, the top where the rate of ultraviolet absorption is also small, since the compatibility over upper resin with a small dissolution rate ratio is low, an addition is restricted. Moreover, although a dissolution rate ratio is comparatively large, since the rate of ultraviolet absorption is large, the light transmission nature to the resist film is uncontrollable in the case of a 4 - t - butoxycarbonyl biphenyl.

[0007] furthermore, in the case of t - butyl KORETO and t - butyl deoxycholate Since the dissolution inhibition effectiveness is inadequate when it uses to Pori (hydroxystyrene) although compatibility is good and excellent as a dissolution inhibitor when it uses to novolak resin the top where the rate of ultraviolet absorption is small When the film decrease phenomenon in which the resist film of a non-irradiating part dissolves to an alkali developer arises, since a raw material is a natural product, supply is unstable.

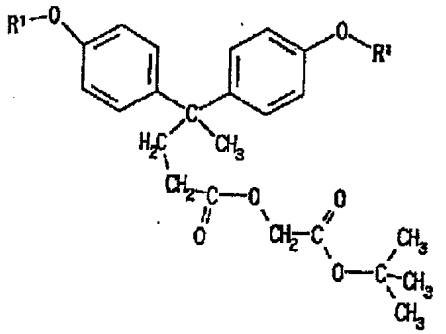
[0008]

[Problem(s) to be Solved by the Invention] Then, this invention person etc. reached header this invention in the new molecular entity which was excellent as a dissolution inhibitor for photoresist, as a result of examining the dissolution inhibitor for photoresist wholeheartedly. Therefore, the purpose of this invention is to offer the new compound which was excellent as a dissolution inhibitor for photoresist which can make dissolution contrast of an exposure section-unexposed part sufficient thing.

[0009]

[Means for Solving the Problem] The above-mentioned purpose of this invention was attained by the diphenolic acid-tert-butoxycarbonyl methyl ester derivative characterized by what is expressed with the following-ization 9.

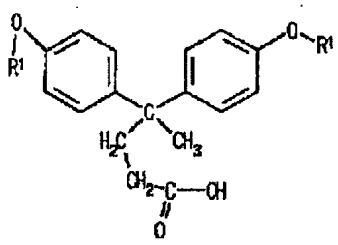
[Formula 9]



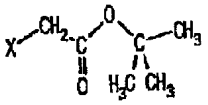
However, R1 in ** 9 Which radical chosen from a hydrogen atom, tert-butyl, a tert-butoxycarbonyl radical, a tert-butoxy carbonylmethyl radical, a 1-methyl-1-methoxy ethyl group, a 2-tetrahydrofuranyl radical, 2-tetrahydropyranyl group, a methoxymethyl radical, and a tert-butyldimethylsilyl radical is expressed.

[0010] The diphenolic acid-tert-butoxycarbonyl methyl ester derivative of the above-izing 9 can be obtained by making alpha-halogenation acetic acid expressed with the diphenolic acid expressed with the following-ization 10 or its derivative, and the following-ization 11 react under existence of a suitable base.

[Formula 10]



[Formula 11]



Although X in ** 11 expresses a chlorine atom, a bromine atom, or iodine atom, it is especially desirable that they are a chlorine atom or a bromine atom.

[0011] Although especially the base used in the reaction of this invention is not limited, specifically, amines, such as alkali-metal salts [, such as a sodium hydrogencarbonate, a sodium carbonate, a potassium hydrogencarbonate, potassium carbonate, a sodium hydroxide a potassium hydroxide sodium methylate, sodium ethylate, and potassium-tert-butyrate,] or triethylamine, diisopropyl monomethylamine, dimethylaniline, pyridine, 4-N, and N-dimethylamino pyridine and 4-(1-piperidino) pyridine, etc. are mentioned. the diphenolic acid whose amount of the above-mentioned base used is a raw material, or its derivative -- receiving -- 1 to 10molEq -- although it can use -- especially -- 1 to 3molEq -- using is desirable.

[0012] Although especially the solvent used in the reaction of this invention is not limited, specifically, aprotic polar solvents, such as halogenated hydrocarbon, such as aromatic hydrocarbon, such as ketones, such as alcohols, such as a methanol, ethanol, propanol, 2-methylethanol, a butanol, and tert-butyl alcohol, an acetone, and a methyl ethyl ketone, benzene, toluene, and a xylene, a methylene chloride, and chloroform, N.N-dimethylformamide, N,N-dimethylacetamide, and dimethyl sulfoxide, etc. are mentioned. An acetone, N.N-dimethylformamide, N,N-dimethylacetamide, dimethyl sulfoxide, etc. are desirable also especially in these.

[0013] Although what is necessary is to be able to perform the reaction of this invention in the range of the boiling point of a solvent from a room temperature, and just to set up reaction time suitably by the reaction condition, generally it ends in 30 minutes - about 24 hours. The diphenolic acid-tert-butoxycarbonyl methyl ester derivative of this invention can be used as usual as a dissolution inhibitor of the chemistry magnification mold resist of three component types, and the resist image of high resolution can be acquired by using this.

[0014]

[Effect of the Invention] When the diphenolic acid-tert-butoxycarbonyl methyl ester derivative of this invention is used as a dissolution inhibitor of a chemistry magnification mold resist and not only definition but sensibility becomes enough since the dissolution contrast between exposure section-unexposed parts is

enough, the configuration of a pattern does not necessarily change with aging.

[Example] Hereafter, this invention is not limited by this although this invention is further explained in full detail according to an example.

[0015] Example 1

28.6g of synthetic diphenolic acid and 4.2g of sodium hydroxides of diphenolic acid-tert-butoxycarbonyl methyl ester were dissolved in the mixed liquor of ethanol 100ml and 20ml of water at 50 degrees C. Bromoacetic acid-tert-butyl 21.8g was added to this and it stirred at 50 degrees C for 8 hours. The solvent was distilled out under reduced pressure after reaction termination. After dissolving residue in chloroform 200g, 100g water washed, the organic layer was dried with sulfuric anhydride magnesium, subsequently it decompressed, the solvent was removed, and the oil-like rough product was obtained. When the silica gel column chromatography separated the obtained rough product, diphenolic acid-tert-butoxycarbonyl methyl ester 25.5g (64% of yield) was obtained as the chloroform-methanol =99:1 elution section.

[0016] This product 1 H-NMR spectrum is as being shown below.

1 H-NMR (CDCl3, Delta)

1.46(9H,s)

1.55(3H,s)

2.2 (2H,dd)

2.42(2H,dd)

4.55(2H,s)

6.72(4H,d)

7.04(4H,d)

[0017] Example 2

After dissolving 28.6g of synthetic diphenolic acid of 4 and 4'-JI (4-tert-butoxycarbonyl methoxypheny) pentanoic acid-tert-butoxycarbonyl methyl ester in dimethyl sulfoxide 200g, 50g of anhydrous potassium carbonate and chloroacetic-acid-tert-butyl 50g were added, and it stirred at 60 degrees C for 4 hours. After reaction termination, after adding and stirring 500g of water, the water layer was removed by the decantation.

[0018] After dissolving the oily matter of residue in chloroform 150ml, 100g of water washed, and the solvent was distilled out after drying a chloroform phase with sulfuric anhydride magnesium. When the silica gel column chromatography separated the obtained rough product, 4 and 4'-JI (4-tert-butoxycarbonyl methoxypheny) pentanoic acid-tert-butoxycarbonyl methyl ester 49.6g (79% of yield) was obtained as a pure substance as the chloroform elution section.

[0019] This product 1 H-NMR spectrum is as being shown below.

1 H-NMR (CDCl3, Delta)

1.44(9H,s)

1.46(18H,s)

1.56(3H,s)

2.18(2H,dd)

2.4 (2H,dd)

4.43(2H,s)4.47(4H,s

6.78(4H,d)

7.05(4H,d)

[0020] Example 3

Diphenolic acid-tert-butoxycarbonyl methyl ester 10g compounded in the synthetic example 1 of 4 and 4'-JI (4-tert-buthoxycarbonyloxy phenyl) pentanoic acid-tert-butoxycarbonyl methyl ester was dissolved in pyridine 50g, and after adding G tert-butyl dicarbonate 13g, it stirred at 40 degrees C for 2 hours. After reaction termination, the water layer was removed, after adding and stirring 200g of water.

[0021] The solvent was distilled out, after dissolving the oily matter of residue in chloroform 50g and drying with sulfuric anhydride magnesium. When the silica gel column chromatography separated the obtained rough product, 10.5g (70% of yield) of 4 and 4'-JI (4-tert-buthoxycarbonyloxy phenyl) pentanoic acid-tert-butoxycarbonyl methyl ester was obtained as the chloroform elution section.

[0022] This product 1 H-NMR spectrum is as being shown below.

1 H-NMR (CDCl3, Delta)

1.46(9H,s)

1.56(18H,s)

1.57(3H,s)

2.2 (2H,dd)

2.4 (2H,dd)

4.46(2H,s)

7.07(4H,d)

7.18(4H,d)

[0023] Example 4

10g of anhydrous potassium carbonate and bromoacetic acid-tert-butyl 20g (102.5mmol) were added to 4 and 200ml acetone solution of 20g (46.5mmol) of 4 'composition 4 and 4 of - JI [4-(1-methyl-1-methoxyethoxy) phenyl] pentanoic acid-tert-butoxycarbonyl methyl ester' JI [-] [4-(1-methyl-1-methoxyethoxy) phenyl] pentanoic acid, and heating reflux was carried out for 8 hours. Liquids were separated, after carrying out reduced pressure distilling out of the acetone after radiationnal cooling and adding 200ml chloroform and water to residue respectively.

[0024] After rinsing an organic layer further, it dried with sulfuric anhydride magnesium and the rough product was obtained by distilling out a solvent under reduced pressure. When the silica gel column chromatography separated the obtained rough product, 19.3g (71% of yield) of 4 and 4'-JI [4-(1-methyl-1-methoxyethoxy) phenyl] pentanoic acid-tert-butoxycarbonyl methyl ester was obtained as colorless oily matter as fractionation eluted under chloroform.

[0025] This product 1 H-NMR spectrum is as being shown below.

1 H-NMR (CDCl3, Delta)

1.4 (9H,s)

1.53(3H,s)

1.57(12H,s)

2.18(2H,dd)

2.38(2H,dd)

3.35(6H,s)

4.45(2H,s)
6.77(4H,d)
7.02(4H,d)
[0026] Example 5
After dissolving diphenolic acid-tert-butoxycarbonyl methyl ester 10g compounded in the synthetic example 1 of 4 and 4'-JI (4-tetrahydrofuran-2-yloxy phenyl) pentanoic acid-tert-butoxycarbonyl methyl ester in 50g of methylene chlorides, 5.3g and pyridinium Para-toluenesulfonate 0.2g were added, and 2 and 3-dihydrofuran was stirred at the room temperature for 6 hours. 50ml of saturation sodium-carbonate water solutions was added and stirred after reaction termination, and, subsequently the organic layer was separated.
[0027] When reduced pressure distilling out of the solvent was carried out, oil-like residue was obtained and the silica gel column chromatography subsequently separated this after rinsing the obtained organic layer and drying with sulfuric anhydride magnesium, 9.7g (72% of yield) of 4 and 4'-JI (4-tetrahydrofuran-2-yloxy phenyl) pentanoic acid-tert-butoxycarbonyl methyl ester was obtained as a chloroform effluent.
[0028] This product 1 H-NMR spectrum is as being shown below.
1 H-NMR (CDCl3, Delta)
1.46(9H,s)
1.55(3H,s)
1.8-2.3 (10H, m)
2.42(2H,dd)
3.9-4.1 (4H, m)
4.45(2H,s)
5.79(2H,m)
6.93(4H,d)
7.13(4H,d)
[0029] Example 6
After dissolving diphenolic acid-tert-butoxycarbonyl methyl ester 10g compounded in the synthetic example 1 of 4 and 4'-JI (4-tetrahydropyran-2-yloxy phenyl) pentanoic acid-tert-butoxycarbonyl methyl ester in 50g of methylene chlorides, 2 and 3-dihydro-2H-pyran 6.3g and pyridinium Para-toluenesulfonate 0.2g were added, and it stirred at the room temperature for 6 hours. 50ml of saturation sodium-carbonate water solutions was added and stirred after reaction termination, and, subsequently the organic layer was separated.
[0030] Oil-like residue was obtained when reduced pressure distilling out of the solvent was carried out, after rinsing the obtained organic layer and drying with sulfuric anhydride magnesium. When the silica gel column chromatography separated the obtained residue, 4 and 4'-JI (4-tetrahydropyran-2-yloxy phenyl) pentanoic acid-tert-butoxycarbonyl methyl ester 10.5g (70% of yield) was obtained as a chloroform effluent.
[0031] This product 1 H-NMR spectrum is as being shown below.
1 H-NMR (CDCl3, Delta)
1.46(9H,s)
1.4-2.1 (12H, m)

1.55(3H,s)
2.2 (2H,dd)
2.42(2H,dd)
3.4-4.0 (4H, m)
5.4 (2H,m)
6.96(4H,d)
7.14(4H,m)

[0032] Example 7

It was dropped having covered [which dissolved tert-butyldimethylsilyl chloride 8.3g in the 50ml tetrahydrofuran] it for 30 minutes stirring at a room temperature, after dissolving diphenolic acid-tert-butoxycarbonyl methyl ester 10g compounded in the synthetic example 1 of 4 and 4'-JI (4-tert-butyldimethylsiloxy phenyl) pentanoic acid-tert-butoxycarbonyl methyl ester in tetrahydrofuran 50ml and adding triethylamine 5.6g and imidazole 0.2g. It flowed back for 2 hours, and after cooling radiationally, it added each chloroform and 100g of water, and liquids were separated. After rinsing an organic layer once again, it was separated again.

[0033] After drying the obtained organic layer with sulfuric anhydride magnesium, reduced pressure distilling out of the solvent was carried out, and oil-like residue was obtained. When the silica gel column chromatography separated the obtained residue, 4 and 4'-JI (tert-butyldimethylsiloxy phenyl) diphenolic acid-tert-butoxycarbonyl methyl ester 10.7g (68% of yield) was obtained as fractionation eluted under chloroform.

[0034] This product 1 H-NMR spectrum is as being shown below.

1 H-NMR (CDCl3, Delta)
0.24(12H,s)
0.88(18H,s)
1.44(9H,s)
1.5 (3H,s)
2.21(2H,dd)
2.42(2H,dd)
4.4 (2H,s)
6.87(4H,d)
7.14(4H,d)

[Translation done.]